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Energy Procedia 79 (2015) 903 – 909

Energy Procedia

2015 International Conference on Alternative Electron in Developing Countries and Emerging Economies

Development of TiO_2/TiO_2-V_2O_5 Compound with Polyaniline for Electron Storage

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Abstract

The polyaniline (PANI) assembled on TiO_2-V_2O_5 compound (TVC) was prepared by in-situ polymerization method. The TiO_2-TVC and TiO_2-TVC/PANI composite films at TVC/TiO_2 molar ratio of 0.1 deposited on the ITO glass successfully prepared using spin coating technique. The products were characterized by using SEM, TGA, FTIR and electrochemical technique. The maximum electron storage of TiO_2/PANI-TVC (2.17 wt % PANI in TVC/PANI) under UV stimulation is 3,689.3 C/mol, which is 30% higher than that of TiO_2-TVC. This electron storage is equivalent to 96.3% of maximum capacity of TVC. This result suggests that optimal amount of PANI effect on higher efficiency of electron storage.

Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE

Keywords: electron storage; photocatalyst; polyaniline ; TiO_2-V_2O_5 compound;

1. Introduction

TiO_2 is known as a photocatalyst which has various remarkable functions including self-cleaning [1], anti-bacterial [2], gas sensor [3], and anti-corrosion [4]. The utilization of TiO_2 is active based on redox reaction of photogenerated electrons and holes that are excited under UV irradiation.

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Peer-review under responsibility of the Organizing Committee of 2015 AEDCEE
doi:10.1016/j.egypro.2015.11.585

However, these applications are workable only under UV light irradiation on TiO_2 surface. The restriction of applications under daylight is an important drawback of TiO_2 which can be eliminated by development of its ability for electron storage. Recently, our group has developed TiO_2-V_2O_5 compound (TVC) that exhibits high capacity of electron storage [5]; however, the coupling TiO_2 and TVC for photo-electron storage gave low efficiency possibly owning to distance barrier of charge transferring between exciting photo-electrons and electron storage sink. Therefore, to bridge the gap of transferring these electrons the in-situ conductive polymer has been developed in our present work.

The polyaniline (PANI) is the most attractive polymer because the preparation is facile and polymeric bulk is inert, stable and insoluble in solvent, especially the polymer exhibits photocatalytic and conductive properties [6]. The optimum amount of additional PANI to TiO_2/TVC electron storage films was investigated in the range of 2.0 to 7.0 wt%.

1. Experimental

2.1. Materials

Univar AR grade titanium isoproproxide, $Ti(OC_3H_7)_4$, titanium commercial grade, P25, vanadium pentaoxide, V_2O_5, nitric acid 65%, HNO_3, Hydrochloric acid 37%, HCl, Absolute for analysis ethanol, $C_2H_5(OH)$, Ammonium persulfate, $(NH_4)_2S_2O_8$, polyethylene glycol (MW 10,000), aniline, $C_6H_5NH_2$, and deionized water.

2.2. Electron storage matter (TVC)

Dissolve titanium (IV) isopropoxide 16.7 ml in to 200 ml of 0.07 M NHO_3 solution and stir at room temperature (20%RH) for 3 days to obtain clear solution. Purify sol TiO_2 by dialysis in deionized water. Mix 90 mg V_2O_5 in 30 ml sol TiO_2 and subsequently 2 hours ultra-sonicate for well mixing to obtain yellowish slurry. Calcine the yellowish slurry to brown powder at 550°C for 1 h.

Charge transferring was improved by PANI assembling on TVC by in-situ polymerization method [7]. Mix TVC 4 g, aniline 0.1 g and $(NH_4)_2S_2O_8$ 226.7 mg in 0.5 M HCl 100 ml and stir for 12 h. Filtrate and wash with ethanol for several times and dry at 80°C for 2 h to obtain TVC/PANI. The amount of PANI consisting in assembled films was adjusted at molar ratio of aniline/$(NH_4)_2S_2O_8$ increasing to 2, 3 and 4 times.

2.3. Film preparation

The TVC coating was prepared by mixing TVC/PANI and PEG (MW 10,000) 20 mg in 6 ml of DI water and subsequently ultrasonicating for 5 min. After mixing, added 200 mg P25 and re-sonicated to obtain blue-green slurry. The indium tin oxide (ITO)-coated glass plate (size 2.5 × 3.5 cm^2, 1 mm thickness) as the substrate for the film was cleaned in Micro-90 and 3 M NaOH before coating. The blue-green slurry was coated on ITO glass at 3,500 rpm for 20 second and then calcined at 350°C for 1 h. All films were fixed the molar ratio of TiO_2/TVC at 0.1.

2.4. Film Characterization

The morphology of the TiO_2-TVC and TiO_2-TVC/PANI films was characterized by scanning electron microscope (SEM). The amounts of PANI on TVC/PANI were investigated by thermal gravitation analysis (TGA) under N_2 atmosphere with a heating rate of 10 °C/min. The electrochemical properties were observed

by conventional electrochemical cell. The sample was set as working electrode, while reference cell was Ag/AgCl electrode and counter cell was platinum electrode.

2.5 Film Measurement

Electron capacity of films was measured by using a digital potentiostat. A voltage recorder was used to monitor the open-circuit potential of the coated electrodes. The light source was a Hg-Xe lamp equipped with a 365 nm band-pass filter. The light intensity was about 5 mW/cm^2 at the sample surface. After the film was exposed to the light, constant current (1μA) electrochemical discharging was carried out in a 0.1 M NaCl aqueous solution. The cut-off potential was -0.1 V versus Ag/AgCl for the electrochemical discharging. Additional films were observed at maximum capacity by charging the potential to -0.4 V versus Ag/AgCl and discharging at the same condition.

3. Result and Discussion

3.1 The Characterization of Physical Properties

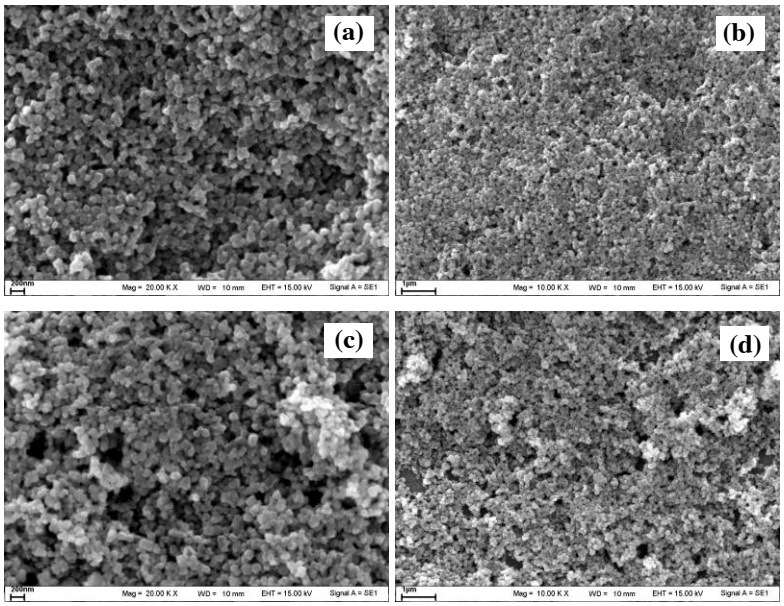

Fig. 1 The SEM micrographs of: (a) TVC at 20,000x ; (b) TVC at 10,000x; (c) TVC/PANI at 20,000x and (d) TVC/PANI at 10,000x.

Figure 1 illustrates SEM images of TVC and TVC/PANI at different magnification. The SEM images showed that as-synthesized samples both are like nano-sphere shape with 100 nm diameter. The porosity of TVC/PANI film is much more than that of TVC film due to a presence of PANI effected on a well-dispersing particles. In addition, advantages of porosity can assist the intercalated cations transferring into the matter and higher surface area. These can improve the electron storage efficiency of films. To confirm higher surface area of TVC/PANI, specific surface area of all samples were measured by BET method. The specific surface areas of TVC and TVC/PANI with various PANI contents were shown in Table 1. The specific surface area of TVC containing 2.17 wt % increased 80% compared with that of PANI-free

TVC plausibly due to the growth of PANI in tortuous TVC pores. The collapsed pores or PANI-fully filled pores may occur while gradually increasing PANI more than 2.17% wt and the lower surface area was obtained.

Table 1. Specific surface area of TVC at various PANI contents

PANI in TVC (wt%)	Surface area (m^2/g)
0	9.0
2.17	16.7
4.41	15.5
5.74	13.8
7.05	13.1

The PANI growth on TVC was investigated by FT-IR technique as shown in Figure 2. The FT-IR spectra indicate functional group of PANI existing in TVC/PANI. The peaks occurring at 1,560 cm^{-1} and 1,471 cm^{-1} in the spectra of synthesized PANI (Figure 2a) and commercial PANI (Figure 2b) correspond to C=N in quinnone and C=C in benzene ring stretching, respectively. Whereas the band at 1,290 cm^{-1} is ascribed to stretching C-N bond locating in quinonoid structure and a secondary aromatic amine presents C-N bond stretching at 1,235 cm^{-1}. The bands occurring at 1,108 and 1,029 cm^{-1} are assigned to C-H bond existing in aromatic ring and the band at 887 cm^{-1} is attributed to a presence of C-H bond locating in 1,4-disubstituted rings [8]. The FT-IR spectra of TVC/PANI composite (Fig.2c) presents the intrinsic absorption peaks of PANI and the peak shifting to blue visible range ascribing to chemical reaction between TVC and PANI.

Additionally, the FT-IR spectra of TVC (Figure 2d) illustrates absorption band of TiO_2 between 400-700 cm^{-1} which was attributed to Ti-O and Ti-O-Ti strething mode [9]. The peak at 1024 cm^{-1} is characteristic of the stretching vibration of the terminal vanadyl, V=O. The bands around 1640 cm^{-1} and the very broad band in the region of 3600-2500 cm^{-1} were assigned to the binding vibration of H-O-H and O-H stretching vibration of thephysically adsorbed water molecules[10].

Decomposition of PANI in TVC/PANI compared with TVC and pure PANI was observed by TGA technique as shown in Figure 3. Operating conditions of TGA are at ramping rate of 10°C/min to final temperature at 600°C under N_2 atmosphere. The TVC only decomposed at 0.8 wt % located at 600ºC while pure PANI decomposed at 48 wt%. These experimental data were employed to calculate the PANI content in the TVC/PANI samples.

3.3 Electrochemical analysis

Electrochemical charge and discharge behaviour of TiO_2-TVC films and TiO_2-TVC/PANI films were investigated. The TVC undergoes the following redox reactions as shown in equation 1-3[11].

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^- + h^+) \quad (1)$$

$$TiO_2\,(h^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \quad (2)$$

$$TVC + xH^+ + xe^- \leftrightarrow H_xTVC \quad (3)$$

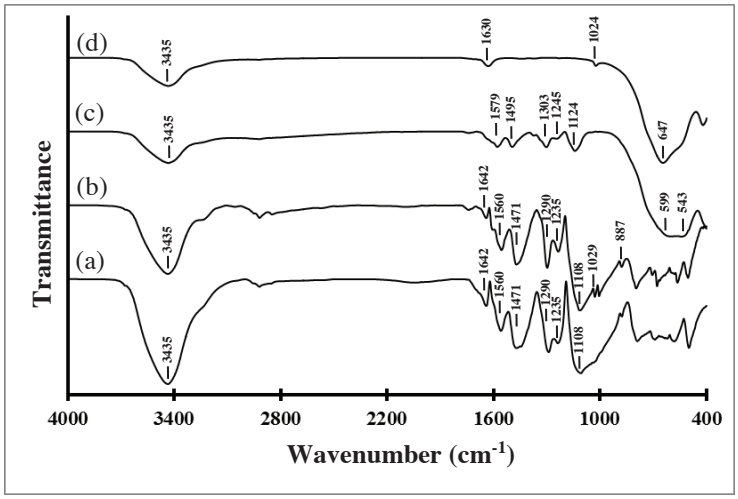

Fig. 2 FT-IR spectra of (a) synthesized PANI, (b) commercial PANI, (c) TVC/PANI and (d) TVC.

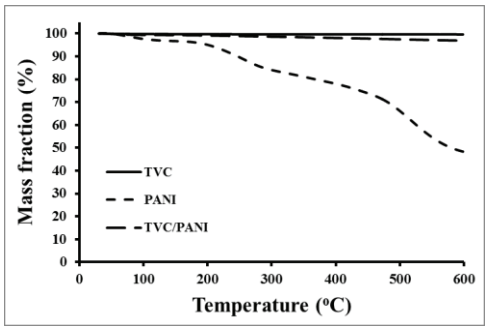

Fig. 3 Thermagravimetric Analysis of (a) TVC, (b) TVC/PANI and (c) PANI.

TiO_2-TVC film and TiO_2-TVC/PANI films were electrochemically charged at −0.4 V versus Ag/AgCl for 3 h and discharged at 1 μA. The fabricated film with PANI seems to have no effect on the electron capacity because the electron capacities of both films are even at 3,830.1 C/mol as shown in figure 4.

However, the electron capacity of TVC-TiO_2 film was only 2,901.5 C/mol, which is 75.8% of maximum capacity, after UV irradiating for 3 h. These indicated the distance barrier of charge transferring between TiO_2 and TVC. The energy storage enhancement was accomplished by coupling of PANI and TVC. It can be seen that the TiO_2/PANI-TVC film composing of 2.17 wt% PANI in TVC/PANI could store electron up to 3,689.3 C/mol which is 96.3% of maximum capacity. However, the larger amount of PANI suppressed the electron transfer.

However, increasing PANI more than 2.17 wt% can inhibit the intercalation of cation transferring from TiO_2 to TVC that can cause the loss of energy storage capacity. This is because the steric hindrance

of longer chain PANI can retard the electron transferring to TVC. This opportunity can cause the electron rebounding to TiO_2 particles.

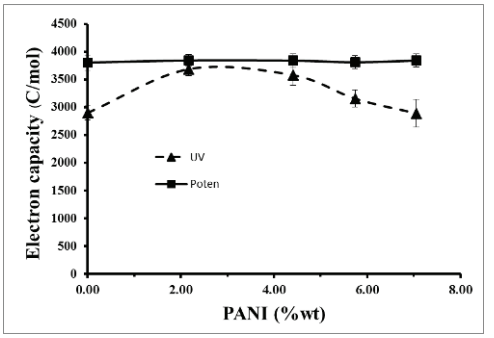

Fig. 4. Electron capacity of TiO_2-TVC/PANI composite films after electrochemical charging (poten) and photo-charging (UV) condition.

4. Conclusion

The amount of PANI varied at 2.17, 4.41, 5.74 and 7.05% in TVC/PANI by weight in fabricated films can facilitate the rate of electron transferring from TiO_2 to TVC and it leads to increase of energy storage efficiency especially from 75.8% to 96.3% for the film composed of 2.17% wt. PANI. This is plausible because of charge transferring via inducing conductive polymer chain as PANI which can accomplish the higher energy storage efficiency. However, the optimum content of PANI was only 2.17 wt% owning to electron-hole recombination for longer PANI chain at higher content.

Acknowledgements

This work has been supported by the Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand through its program of the Center of Excellence Network.

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